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Synthesis of Norbornadiene-Containing Polyamide Based Polymer

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Synthesis of polyamide-based polymer containing norbornadiene was aimed in this study. Aromatic group containing cyclopentadiene was synthesized primarily. Cyclopentadiene was converted to cyclopentadienyl anion through the reaction with metallic sodium. Substituent containing aryl group was linked to the 5-position of cyclopentadiene by reacting the resulting anion with halide compound. Diethyl 7-arylmethyl-2,5-norbornadiene-2,3-dicarboxylate monomer was synthesized by [4 + 2] (Diels Alder) cycloaddition reaction of substitute obtained this way with cyclopentadiene diethyl 2-butyndioate. By activating this synthesized monomer with diaminoethane, targeted polyamide-based polymer containing norbornadiene was reached. Changes in functional group in the polymerization reaction were monitored by FTIR spectroscopy technique. Moreover, in order to clarify the structure of the polymer obtained, IR and ^{1}H NMR spectra were recorded.

Keywords: Norbornadiene, Quadricyclene, Energy storage, Polyamides.

INTRODUCTION

A different approach to absorb the light energy is to use the groups which absorb the light energy reversibly and release this absorbed energy by returning again to the original structure. Researches continue in our laboratory in order to improve polymeric materials capable of converting light into chemical energy in a systematic manner [1]. Within these, reversible photo-regulation from norbornadiene to quadricyclene has attracted great interest. Because photo-energy is stored in quadricyclene molecule as tensile energy (approximately 96 kJ/mol) and then it can be retrieved [2]. This photo-isomerization reaction in which electron exchange occurs is also called valence isomerization. Because of this feature, many polymers have been prepared with norbornadiene parts as suspended groups attached to chain structure (pendant).

Nishikuba and his group [3] synthesized new photosensitive polymers containing N,N-disubstituted amide groups and pendant norbornadiene moieties with high conversion. They found that the polymers can store approximately 80-86 Kj/mol energy. Nagai *et al.* [4] synthesized polymers having trifluoromethyl substituent norbornadiene moieties on main chain and side chains.

These polymers demonstrated a broad absorption bands in the visible light spectra and norbornadiene moieties in these polymers isomerized very fast (Fig. 1).

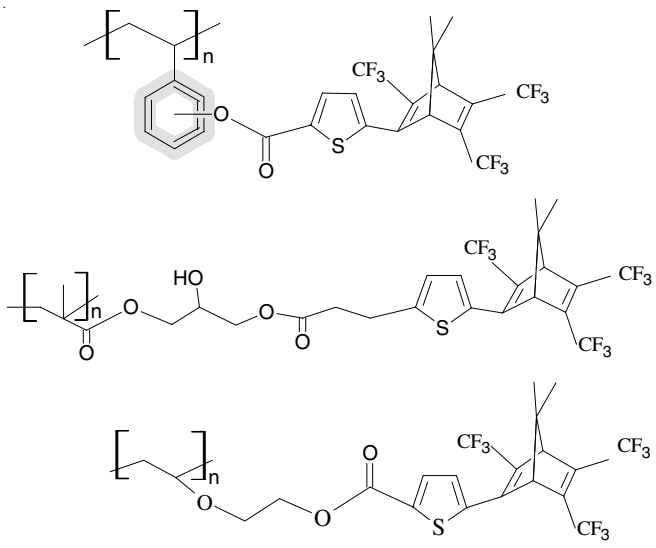


Fig. 1. Some polymers belonging to trifluoromethyl substituted norbornadiene parts

Kawatsuki *et al.* [5] synthesized styrene polymers with pendant norbornadiene groups attached to amide chain (Fig. 2). Here, R is substituted aniline group ring attached over methoxy or nitrogen or other position. These pendant groups reversibly transform to quadricyclene units in polymer films when they are exposed to ultraviolet light on two different wavelength.

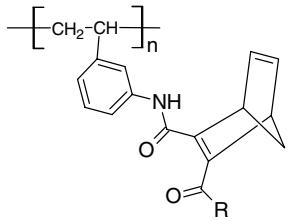


Fig. 2. Norbornadiene-structured styrene polymers attached to amide chain

These materials displayed photosensitivity as high as transition red shift in absorption spectra under the light propagation [6].

Sampei *et al*. [7] obtained polyesters as a result of reaction of 2,5-norbornadiene-2,3-dicarboxylic acid diglycidyl ester with adipol chloride. They found that photochemical reaction rate in polymer properties was higher than the one in side chain when photochemical embodiment of norbornadiene parts was conducted in polymeric films [7].

EXPERIMENTAL

Chemicals used in the experiment are analytically pure and they are the products of companies such as Merck and Aldrich. The solvents used are diethyl ether, acetone, methanol, hexane, benzene, toluene, chloroform and tetrahydrofuran. Benzene and tetrahydrofuran were purified by drying and distillation. Infrared spectra of synthesized compounds were taken in Selcuk University Faculty of Architecture and Engineering Department of Chemical Engineering and results of ^{1}H NMR analysis were taken with Varian (400 MHz) ^{1}H NMR device in R&D Center of Selcuk University.

Synthesis of cyclopentadiene from dicyclopentadiene: 200 mL of mineral oil was placed in 500 mL flask whose necks were equipped with thermometer, separation head and a dropping funnel. The temperature of the flask content was increased to 220 °C. Dicyclopentadiene was added to the flask drop wise from a separatory funnel. Cyclopentadiene formed by decomposition of dicyclopentadiene was taken by distillation and stored at -20 °C (b.p.: 43 °C) (Fig. 3).

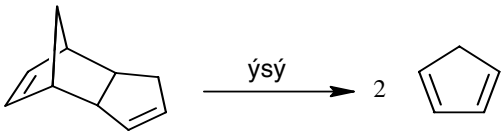


Fig. 3. Synthesis of cyclopentadiene from dicyclopentadiene

Synthesis of diethyl 7-(4-methyl benzyl)bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate: 6.6 g (0.1 mol) cyclopentadiene and 180 mL dry tetrahydrofuran was put into 250 mL flask whose necks were equipped with a reflux condenser and a pressure-balanced dropping funnel. The reaction medium was allowed to keep 0 °C by cooling the flask externally with ice bath. 2.3 g (0.1 mol) metallic Na was added on cyclopentadiene. A yellow solution was obtained together with the presence of hydrogen gas. After the completion of gas release, 14 g (0.1 mol) of 4-methylbenzyl chloride was added to the mixture and it was stirred at 0 °C for 1.5 h and then filtered. Yellow solution was dried at the same temperature under reduced pressure. The resulting residue was purified using column chromatography. Toluene/ethyl acetate mixture with 1/5 volume ratio was used as mobile phase and silica gel 60 was used as stationary phase for the method. Eluents were collected as 10 mL fractions, same ones were combined and they were separated under the vacuum. 5-(4-Methylbenzyl)-1,3-cyclopentadiene was obtained as a product.

A mixture of 100 mL dry tetrahydrofuran and 17 g (0.1 mol) diethyl 2-butindioate was placed into 250 mL flask. 0.1 mol (17.0 g) 5-(4-methylbenzyl)-1,3-cyclopentadiene was added, N_2 gas was passed through the system at the same time while the solution was stirred with a magnetic stirred. Then, the temperature of the flask was raised to 80 °C by heating with the help of oil bath. By continuing to pass N_2 gas from the system at this temperature, magnetic stirrer was continued to the reaction for 24 h. Tetrahydrofuran was removed in the evaporator. The resulting residue was purified using column chromatography. Toluene/ethyl acetate mixture with 1/5 volume ratio was used as mobile phase and silica gel 60 was used as stationary phase for the method. Consequently, diethyl 7-(4-methyl benzyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate was obtained as product (Fig. 4).

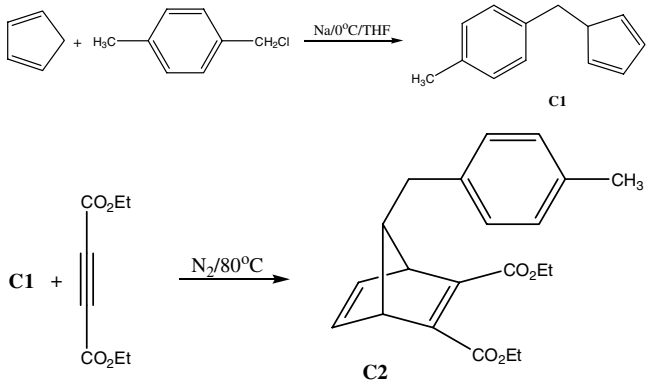


Fig. 4. Synthesis of diethyl 7-(4-methyl benzyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate

Synthesis of ethyl 7-(4-methyl benzyl)bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate-diaminoethane copolymer: Diaminoethane (50 mL) and 34 g (0.1 mol) diethyl 7-(4-methylbenzyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate mixture was stirred with a magnetic stirrer and reacted under N_2 atmosphere and condenser. The reaction was continued at 110 °C for 2 days, complete depletion of diethyl 7-(4-methylbenzyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate was determined by TLC. The brown solid product was observed to settle down. All unreacted diaminoethane was allowed to pass to aqueous phase by the addition of excess 5 % HCl to the reaction mixture. It was filtered and washed with distilled water. The residue was dried for 24 h (Fig. 5).

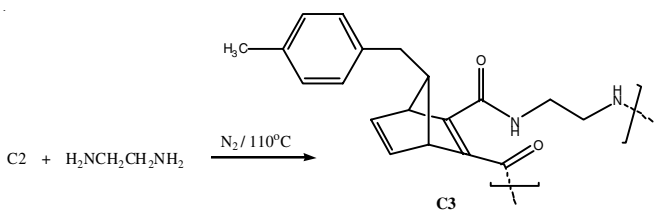
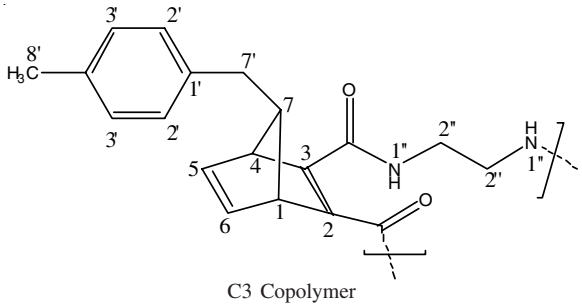


Fig. 5. Synthesis of diethyl 7-(4-methyl benzyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-diaminoethane copolymer

In the IR spectrum of the synthesized polyamide copolymer C3 (Fig. 6); single signal at 3256 cm^{-1} is originated from amide N-H (1") stretching vibration. The bands observed at 3010 cm^{-1} are the stretching bands belonging to C-H bonds present in aromatic ring and double bond in norbornadiene residue. The bands observed at 2921 and 2880 cm^{-1} are aliphatic C-H stretching band. The band at 1613 cm^{-1} is absorption band belonging to C=O vibrations (amide-I band). The signal at 1539 cm^{-1} belongs to N-H stretching (amide-II band). The signal at 1471 cm^{-1} belongs to stretching vibration of aromatic C=C double bonds. The signal at 1320 cm^{-1} belongs to C-N stretching (amide-III band) vibration. The signal at 763 cm^{-1} is out-of-plane aromatic C-H bending bands. The bands observed in the spectrum are compatible with the structure of copolymer.



C3 Copolymer

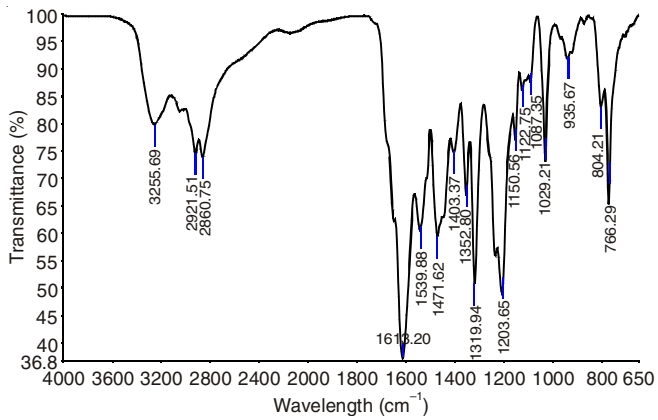


Fig. 6. IR spectrum of C3 copolymer

IR spectrum (KBr, ν_{max}, cm^{-1}): 3255 (N-H), 1613 (C=O), 1320 (C=N), 1539 (N-H), 1471 (C=C), 2921 (C-H).

^{1}H NMR (400 MHz; $CDCl_3$) ppm; 7.20 (d, 2H), 7.10 (d, 2H), 3.70 (d, 1H), 3.60 (d, 1H), 3.47 (broad signal 1H), 2.85 (M, 2H), 2.73 (M, 2H), 2.65 (m, 2H), 2.35 (s, 3H).

RESULTS AND DISCUSSION

In this study, synthesis of polyamide-based polymer containing norbornadiene was aimed by binding of aryl group to cyclopentadiene compound. In cyclopentadienyl sodium and aryl halide reaction, 0 °C was found to be more appropriate. Diels Alder reaction of the resulting cyclopentadiene derivatives with acetylene dicarboxylate was found to occur at 110 °C.

As a result, copolymer having polyamide structures with norbornadiene moieties, which is thought to play an important role in the storage of solar energy, was synthesized. The synthesized polymers are considered to be capable of storing solar energy as chemical energy.

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